Recent Discoveries in Physical Science—III*

Chemical Valency Bonds Interpreted as Electric Lines of Force

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THERE are many compounds, of which ordinary copper sulphate is an example, in which the molecule is a combination of two systems, each of which is capable of existing by itself in the free state. The molecule of copper sulphate in its ordinary condition can be represented as

Of this combination, the system CuSO_4 can exist by itself, and the H_2O is, of course, also stable when alone. Each, in fact, constitutes in itself a saturated compound with the valencies of all the atoms satisfied. The existence of the molecule $\text{CuSO}_4 + 5 \text{H}_2\text{O}$ shows, however, that, even so, the two systems still possess the power of forming compounds by the action of what are sometimes known as residual affinities, or, as Werner calls them, "auxiliary valencies." These auxiliary valencies can bind together one molecule to another, thus forming additional compounds. The auxiliary valencies differ from the ordinary valencies in that the ordinary valencies bind one atom to another, or to a radical, while the auxiliary valencies are only able to bind together molecules, and cannot bind atoms. Compounds formed by the exercise of these auxiliary valencies are therefore sometimes known as molecular compounds. Whatever the origin of this power, it cannot be expected to bind an ordinary atom, since it cannot "saturate" that atom, and the result will be that the unsaturated valencies of the latter will combine with another atom on the first opportunity.

Compounds bound together by auxiliary valencies have quite definite properties. The molecule $\text{CuSO}_4 + 5 \text{H}_2\text{O}$ has, in fact, properties quite different from the molecule CuSO_4 and from the molecule H_2O . Such molecular compounds are in most cases very fairly stable. Thus ordinary copper sulphate has to be heated to 100 deg. Cent. before it loses any of its combined water, and up to 200 deg. Cent. before the water can be entirely driven off. When CuSO_4 is in combination with water it has, as stated, entirely different properties from what it possesses when free from water. One of the properties most frequently altered is the color. The attraction of water to the dry molecule produces in certain cases remarkable changes of color. Thus, anhydrous cobalt chloride is blue, while when the molecule combines with water the color is pink.

It is difficult to draw a line between molecular compounds and the ordinary chemical compounds in which the constituents of the molecule are held together by the ordinary chemical valencies. A remarkable feature is, however, that in every case of a molecular compound one, at least, of the molecules concerned has its atoms charged with electricity. Water is a typical example of such a compound, but alcohol and ammonia are other instances of compounds having charged molecules, and capable therefore of forming molecular compounds. Molecules having charged atoms are able to exert a much stronger external field than can molecules in which the component atoms are neutral, and in which when entering into the combination there is merely a displacement of the electricity on the surface of the atom, and not a transference of a charge from one atom to another.

The external force exerted by the water molecule, in which the hydrogen is positively charged and the oxygen negatively, is accordingly much greater than that which is exerted by marsh gas (CH_4), in which neither the hydrogen atoms nor the carbon atom carry charges.

The laws governing molecular combinations have been studied by many chemists, and especially by Werner. They are found to be somewhat analogous to those which hold in the case of the ordinary valencies. As to the latter the carbon atom, for example, cannot hold more than four atoms of hydrogen, four of chlorine or an equivalent number of other atoms. There is a similar limit to the number of molecules which can be held in molecular compounds. This is what might be expected from very general considerations indeed. For instance, the molecule of HCl has charged atoms, and can therefore attract like a magnet. If placed in water, a molecule of water will be attracted to the hydrogen, say, and being the first to arrive, will attach itself in the position with the strongest field. When a second molecule comes up and also attaches itself to the hydrogen atom, it will push the other about a little, so that neither occupies quite the best position in which the

attraction is strongest. Neither, therefore, will be held quite so strongly as the first molecule was initially. When a third molecule of water comes up and also hangs on to the hydrogen atom, the bond will be still weaker. With every addition the hold gets weaker and weaker till it becomes insufficiently good to withstand the collisions from other molecules to which the system is continuously being subjected. It is natural, therefore, to expect a limit to the number of molecules that can be held by the auxiliary valencies. There is a similar attraction of water molecules to the chlorine atom of the HCl , so that ultimately there is a bundle of water molecules hanging on to each atom of the hydrochloric acid molecule, and hence the final resultant compound molecule may be quite large. The size is limited only by the number of molecules which can attach themselves in this way to an atom. Werner reached the conclusion that the maximum number in any one bundle did not exceed six.

The avidity with which water molecules, in suitable conditions, rush to attach themselves to other molecules can be easily illustrated.

[Taking a glass vessel with a little water at the bottom, and filled with SO_2 above, the lecturer showed that, on passing a powerful beam of light through it, a cloud was formed, owing to the condensation of the moisture on the molecules of SO_2 . He also showed an experiment due to Prof. Townsend, in which electrolytic oxygen was allowed to bubble up into a vessel traversed by a powerful beam of light, and showed again that a cloud was formed by the condensation of moisture on the gas.]

One point about these molecular compounds is that

the addition of other molecules may facilitate the charging up of the atoms in the original molecule, so that greater changes may be produced than would be due to the sum of the properties of the two individual molecules. This can be exemplified by the case of sal ammoniac, formed by the action of ammonia on hydrochloric acid. Both NH_3 and HCl are compounds in which the constituent atoms are charged. When such compounds form molecular combinations there is a tendency for the ammonia to drag the hydrogen away from the chlorine in the hydrochloric acid, and dissociation of the latter may occur accordingly, the result being a mixture of the various constituents in a condition of statical equilibrium.

Another difference between the compounds with charged and those with uncharged atoms may prove to be of some importance from the chemical standpoint. The physical properties of water and of marsh gas are very different indeed, and it is of interest to see whether there is any corresponding difference in the laws by which such different classes of compounds are formed. In other words, are the effective valencies the same in compounds with charged atoms (ionic compounds) as in cases in which the atoms carry no charges. I hope to give reasons for showing that there is a very distinct difference in the two cases. Certain compounds are possible under the valency law when the atoms are not charged which are not possible when the atoms carry charges. The latter, the ionic compounds, obey the ordinary valency laws of the chemist. If however, the atoms are uncharged, we can get, in addition to the ordinary compounds, others formed in accordance with an extension of the usual valency law.

In discussing this matter it is necessary to form some physical conception of what valency really corresponds to. I take it that each atom contains certain negative corpuscles. Of these some are firmly fixed at the core of the atom, and take no part in any chemical reaction. There are, however, other corpuscles on the surface free to move about and set themselves into position

under external electric fields. It is these mobile corpuscles which enable one atom to hold on to another, and form the material of the bond between the two. The valency is equal to the number of these mobile corpuscles, so that in a univalent element there is one such mobile corpuscle, in divalent elements there are two, in trivalent three, and so on up to seven mobile corpuscles. With eight corpuscles in the outer ring, however, we get a rigid system, in which the corpuscles cannot move relatively to one another.

The mobility of these negative corpuscles is the essential condition for one atom to exert any considerable attraction on another. Suppose, then, we had an atom with one free corpuscle, as represented diagrammatically in Fig. 1, with its negative corpuscle at A. If another such atom were brought near it, with its negative corpuscle at B, repulsion would ensue; but the corpuscles, being free to move, would be driven round to the other side as indicated in Fig. 2, and the positive charge of this second atom being now the nearer to the negative corpuscle at A, attraction would ensue, the initial repulsion being momentary only. In such a case the final result would therefore always be an attraction whatever were the initial conditions.

If, however, the corpuscle in the atom were fixed, it could not be swung round without carrying with it the whole of its atom. This atom is quite a heavy body, difficult to move, while the negative corpuscle has almost no inertia, and can, therefore, if free, be driven round at once.

Hence when the negative corpuscles are mobile the atoms hold each other together, but when fixed they attract each other to a very much less extent. An atom is saturated when it has all its negative particles fixed, the satisfaction of a valency being essentially the fixing of one of the mobile negative particles.

[The difference in the attraction exercised by mobile and by fixed doublets the lecturer illustrated by means of a series of small magnets. It was shown that when these were resting at random on a suspended tray, there was very little resultant attraction when a powerful electro-magnet near by was excited, while the attraction was large when the magnets were mounted on pivots, and were thus free to move round and set themselves.]

Each negative particle in an atom is the origin of a tube of force. If the atom is alone, the tube of force returns into the atom and ends on the positive charge, as indicated diagrammatically in Fig. 3. In such a condition the negative corpuscle remains quite free to move. If, however, the tube of force terminates on some charge external to the atom, the corpuscle will be fixed. This condition is represented in Fig. 4, and the particle is then deprived of its mobility and is unable to attract another atom.

Suppose next that the second atom is neutral, then there will be a similar tube of force from it to the first atom, as indicated in Fig. 5. In fact, with uncharged atoms, for each line of force which leaves an atom there must be a return line, as many coming in as go out. If the atoms are divalent, then two lines of force will leave each and two return, so that the total number of tubes of force between the two is in such cases always double the number of valency corpuscles.

Suppose, however, that a corpuscle passed from one atom to the other, so that one atom became positively and the other negatively charged. As the corpuscle left it would follow its tube of force, which would thus shrink up into the interior of the second atom, and the condition of affairs would then be that represented in Fig. 4, but with only one tube of force between the atoms. In compounds with charged atoms, therefore, the number of lines of force between the constituent atoms is only equal to the chemical valency, while it is double the valency when the atoms are uncharged. The tube of force is, in short, the chemist's bond, which he represents by a bar, thus:

With divalent atoms the chemist writes, for example:

and the bars again represent simply lines of force. The chemist, however, makes no distinction in the number of lines, whether the atoms of the compound carry charges or not, taking the number in both cases to be equal to the valency.

This, however, is only true if the atoms are charged, the number of lines of force being doubled when the

* Third of a series of lectures delivered at the Royal Institution.

atoms of the compound are neutral, and the theory here proposed differs in this respect from the chemical view. It might be thought that this would make no difference, but, as a matter of fact, in the scheme suggested, certain combinations become possible, which are impossible on the old chemical theory. Take, for instance, H_3 . Hydrogen is univalent, and, according to the chemist's view, we could not have such a combination as

since in this diagram two lines of force are represented as issuing from each hydrogen atom. On the other hand, ozone is quite possible from the chemical standpoint, oxygen being divalent. Ozone can be represented as:

On the view I have now brought forward the compound H_3 is, however, quite possible if its constituent atoms are uncharged, since in that case there would be two lines of force to each hydrogen atom, one line of force coming in and one going out.

It will be seen, therefore, that on this view many compounds are possible which are incompatible with the ordinary theory. Benzene, for example, is a famous instance of the difficulty of reconciling the ordinary views as to the valency with the constitution of the molecule.

It is ordinarily represented thus:

Here each carbon atom is represented with three

valencies only, and the difficulty is to dispose of the fourth. Kekulé suggested that the fourth valencies were arranged as indicated below:

There are then, it will be seen, four lines from each carbon atom. This, however, leads to difficulties, since it will be seen that the molecule thus constituted is not perfectly symmetrical, and the more chemists have worked at benzene the more convinced they have become of its perfect symmetry. Armstrong has accordingly suggested the constitution:

Here the fourth affinity is put into a kind of reserve fund at the center of the molecule, and is not ordinarily utilized. This device restores the symmetry of the benzene ring, though it gives no very clear idea as to what becomes of the fourth affinity.

On the hypothesis I have put forward the difficulty disappears. Benzene is a molecule with its atoms uncharged. Hence there are eight and not four lines of force associated with each carbon atom, and two and not one line of force associated with each of the hydrogen atoms. The constitution can, therefore, be represented as shown in the following illustration:

This arrangement satisfies all the valency conditions,

and leaves the ring perfectly symmetrical. It does not conflict with the ordinary chemical view, but extends this by the hypothesis that when we are dealing with compounds having uncharged atoms the lines of force between the constituents are doubled.

In times past I have been inclined to think that chemists were disposed to make excessive use of structural formulæ in which the forces binding the molecule together were represented by lines. I must confess, however, that I am now greatly impressed with the utility of this device, even when used by the chemists I had suspect of pushing it to extremes. From a physical standpoint I now believe that these bonds really represent something with a physical basis at the bottom, though formerly I had been inclined to believe that such formulæ were often artistic rather than scientific. I am, however, now convinced that the chemist's bonds do really represent actual lines of force.

On the new view certain compounds would be capable of existing which are as yet unknown. This objection, however, applies equally to the older view. The valency laws, in fact, merely show the possibility of certain compounds, but give no data as to their stability. The architecture of compounds, constituted according to these laws, might therefore be correct, but the resultant edifice might be unstable as to structure. For example, molecules can exist with unsaturated affinities, because the effect of the molecular collisions may suffice to keep them from combining, even though they have a certain tendency so to do. This can be illustrated with N_2O_4 , which splits up into NO_2 as the temperature is raised, as is shown by the change in the color of the gas. (To be concluded.)

Experimental Evidence of Molecular Structure

At a recent meeting of the Physical Society, Prof. R. W. Wood delivered a lecture on "The Molecular Vibrations Excited by Light-Waves," and pointed out that he had studied them because he had wished to try and find out the mechanism of molecular structure. The most important conclusion at which he had arrived from his researches was that what was ordinarily called absorption by vapors and gases was not really absorption at all, but a scattering or diffraction of the light in all directions by the molecules. In this lecture, he proposed to deal with the illumination or fluorescence of vapors and gases resulting from their illumination by ultra-violet light. At the ordinary room temperature, mercury gave off an exceedingly attenuated vapor, which, when illuminated by the ultra-violet light from the mercury arc, emitted ultra-violet light of the same wavelength as that of the illuminating beam. He described how, working on this principle, he had constructed a new type of lamp, which he called a resonance lamp, by means of which several curious effects could be produced. The peculiarity of the light emitted was its extreme purity. It was much more nearly homogeneous than the light constituting the spectrum lines of the metallic arc. The mercury resonance lamp consisted of a bulb of fused quartz, highly exhausted, and containing a small drop of mercury. The mercury vapor in the bulb was then at a pressure of 1/760,000 of that of the atmosphere, and became strongly luminous when the light from a mercury arc-lamp was focussed upon it. The light emitted was invisible to the naked eye, and could only be detected by photography. In fact, what had been done in the experiments was to focus invisible light on invisible vapor, and to photograph the invisible light that came off the invisible vapor. So nearly was the light homogeneous that it was possible to photograph by it the vapor arising from a drop of mercury placed in a cylinder, and heated to 5 degrees above the room temperature, appearing in the picture as a black smoke. A small flask of transparent quartz containing a drop of mercury when illuminated by light from this lamp appeared as if filled with ink. This resulted from the facts that the light from the resonance lamp was exactly synchronous with the natural vibrations of the mercury molecules, and that they responded in the same way that a tuning-fork responded to a sound equal in pitch with its own.

Photographs of the resonance lamp showed that if the silica bulb was gradually heated, the luminosity, instead of being uniformly distributed throughout the cone of the exciting light, retreated to the front wall of the bulb until it was eventually confined to a thin layer of vapor. The reason was that at higher densities, the waves of light were stopped, and then re-emitted in all directions by the mercury molecules before the light had penetrated

to a depth of more than a small fraction of a millimeter. Sodium vapor might be used instead of mercury. A glass bulb was highly exhausted, and pure metallic sodium placed in it. When the temperature in the flask reached about 200 deg. Cent., the image of a sodium flame thrown on it became visible on the vapor in sharp outline, just as if it had been received on white paper. Experiment had shown that if the sodium light was pure enough, the refractive or diffractive power of the vapor was nearly as great as that of white paper, though as colorless and transparent as air when viewed by ordinary daylight. What could only be detected photographically, in the case of mercury, could be seen by the naked eye in the case of sodium. The increase in the density of the vapor in the flask might be compared roughly with the optical behavior of milky water and milk. A beam of light would pass through milky water, but would be stopped by milk. As was well known, the vapor of sodium gave yellow light

Fig. 1.—When the silica bulb is heated, the luminosity, instead of being uniformly distributed through the cone of exciting light, becomes confined to a thin layer (shown in black) at the surface of the bulb.

Fig. 2.—If the incident light allowed to fall on a bulb containing sodium vapor consists of the broad D_1 and D_2 lines of the sodium spectrum, the light re-emitted from the bulb is much purer, consisting only of the central core of the D_1 and D_2 lines, as indicated in this diagram.

of two different wave-lengths, the D lines. In collaboration with M. Dunoyer, said Prof. Wood, he had shown that in illuminating sodium vapor by the light of one of these yellow lines only, it was possible to get sodium vapor emitting only one D line, a fact that proved that the atomic mechanism that gave rise to these lines was not connected. This result was contradictory to the experiments undertaken with other vapors, in which the excitation of one line by monochromatic light caused the re-emission, not only of the same wave-length, but of a large number of other wave-lengths, bright lines appearing at regular intervals.

STIMULATION BY LIGHT-WAVES.

Experiments were also described, in which such gases

as oxygen and nitrogen had been caused to emit ultra-violet light as the result of stimulation by light-waves that were probably shorter than any previously known. These waves were given out by the electric spark between metallic terminals, but proceeded only a short distance in air, being very rapidly absorbed. The shortest wave-lengths previously known had been described by Schumann. They were completely absorbed by quartz, but passed readily through a considerable thickness of fluorite. While these new waves would pass through a fluorite plate one millimeter thick, they were reduced in intensity to about 2 per cent of their original value. The light emitted by the gases, owing to the shortness of the wave-length, was in most cases invisible, though iodine vapor emitted a green light, if mixed with nitrogen and subjected to the rays, remaining dark, however, if mixed with oxygen. Ordinary air, when stimulated by these waves, gave out a light which the spectroscope showed to be identical with the ultra-violet light emitted by the oxy-hydrogen flame. The advantage of studying the spectra by these methods was that in many cases they could be much simplified, and the relation between the lines brought out. The best illustration of this was the fact already described that it was possible by this method of working to cause sodium vapor to emit one only of the two characteristic yellow lines of the sodium flame.

The study of the structure of the molecule by means of the spectroscope, the lecturer said, might be likened to the attempt on the part of an individual who had no experience with or conception of any musical instrument to get a clear idea of all the musical instruments of an orchestra by listening to a concert, or an attempt to form an idea of a piano by listening to the sound which it gave out when falling downstairs. Methods of exciting radiation such as the spark, the arc, and the flame excited all the lines simultaneously, the acoustic analogy of which was to sound the piano by sitting on the keyboard. Optical methods of exciting radiation corresponded to the striking of a single note at a time on the piano. The most important result of his investigations on these lines had been the establishment of the fact that what was ordinarily called absorption by vapors and gases was not absorption at all, but a scattering or diffraction of the light in all directions by the molecules. On looking at a light through the vapor black absorption lines were seen, because the vapor had diverted the light from the original beam, and thrown it in all directions. It was then possible to pass by gradual stages from this molecular scattering to true absorption, where light was transformed into other forms of energy, either by increasing the density of the vapor itself, or by mixing it with some chemically-inert gas, the absorption appearing to be brought about in some way as a result of molecular collisions.

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